$Mo(\eta^5\text{-}C_5H_4CO_2Me)(CO)_3I$. To a solution of $[Mo(\eta^5\text{-}C_5H_4CO_2Me)(CO)_3]_2$ (0.2 g) in chloroform (40 cm^3) in a Schlenk tube was added dropwise iodine (0.16 g) in chloroform (20 cm^3). The mixture was shaken for 30 min and then washed with aqueous thiosulfate ion (three times) to remove iodine. The organic phase was then separated and dried and on evaporation afforded a solid. This was recrystallized from a hexane/chloroform mixture (1:1 v/v), affording orange-red flakes of the complex (yield 0.2 g).

Acknowledgment. A.C. and N.E.M. wish to thank Professor J. A. McCleverty for advice and the DGRST for financial support.

Registry No. $(n\text{-}Bu_4N)(C_5H_4CO_2Me)$, 74449-25-5; $(n\text{-}Bu_4N)[Mo(\eta^5\text{-}C_5H_4CO_2Me)(CO)_3]$, 74466-22-1; $(n\text{-}Bu_4N)[W(\eta^5\text{-}C_5H_4CO_2Me)(CO)_3]$, 74482-37-4; $Mo(\eta^5\text{-}C_5H_4CO_2Me)(CO)_3CH_3$, 73249-51-1; $[Mo(\eta^5\text{-}C_5H_4CO_2Me)(CO)_3]_2$, 74466-23-2; $Mo(\eta^5\text{-}C_5H_4CO_2Me)(CO)_3I$, 74482-38-5; $[(CH_3COC_5H_4)W(CO)_3]^-$, 74466-24-3; $(CH_3COC_5H_4)W(CH_3)(CO)_3$, 73249-59-9; $[(CH_3COC_5H_4)W(CO)_3]_2$, 74466-25-4; $(CH_3COC_5H_4)W(I)(CO)_3$, 74466-26-5; $(CH_3CO_2C_5H_4)W(CH_3)(CO)_3$, 73243-43-3; $[(CH_3CO_2C_5H_4)W(CO)_3]_2$, 74466-27-6; $(CH_3CO_2C_5H_4)W(I)(CO)_3$, 74466-28-7; $[(CH_3COC_5H_4)Mo(CO)_3]^-$, 74466-29-8; $(CH_3COC_5H_4)Mo(CH_3)(CO)_3$, 73243-46-6; $[(CH_3COC_5H_4)Mo(CO)_3]_2$, 74482-39-6; $(CH_3COC_5H_4)Mo(I)(CO)_3$, 74466-30-1; $Fe(C_5H_4CO_2Me)_2$, 1273-95-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_3(DMF)_3$, 59561-69-2; MeI, 74-88-4; I_2, 7553-56-2.

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Guelph Campus, University of Guelph, Guelph, Ontario, Canada N1G 2W1

Preparation and Characterization of Platinum(II) Complexes Pt(P-C)LX, Where (P-C) Is Metalated Tri-*tert*-butylphosphine

H. C. CLARK,* A. B. GOEL, R. G. GOEL,* and S. GOEL

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Reaction of tri-*tert*-butylphosphine with *trans*-$PtCl_2(NCPh)_2$ in a 2:1 molar ratio in dichloromethane results in the formation of the chloro-bridged dimeric complex $[PtCl(t\text{-}Bu_2PCMe_2CH_2)]_2$ (**2**) along with *trans*-$PtCl(t\text{-}Bu_2PCMe_2CH_2)(P\text{-}t\text{-}Bu_3)$ (**1**) and $(t\text{-}Bu_3PH)Cl$. Complex **2** is also prepared by displacing $t\text{-}Bu_3P$ from complex **1** by reaction with mercuric chloride in benzene. Reaction of complex **1** with $PtCl_2(NCPh)_2$ also produces the dimeric complex **2**, when the reaction is carried out in refluxing benzene. Bridge-splitting reactions of **2** with various ligands give the complexes $PtCl(t\text{-}Bu_2PCMe_2CH_2)(L)$ (**5**) (where L = pyridine, CO, Me_2S, $AsPh_3$, Ph_3Sb, Ph_3P, Et_3P, Ph_2MeP, $i\text{-}Pr_3P$, $c\text{-}Hx_3P$, $t\text{-}Bu_2MeP$, $t\text{-}BuPh_2P$, and $t\text{-}Bu_3P$) which have been characterized by elemental analyses as well as proton and ^{31}P NMR spectral studies. The trans configuration of complexes **5** containing two nonequivalent phosphine ligands is established by the large phosphorus–phosphorus couplings ($J(PP')$) of the order of $\simeq$400 Hz.

Introduction

The intramolecular metalation which occurs between the metal and the C–H bonds of *tert*-alkyl- or arylphosphines in palladium or platinum complexes results in the formation of metal–carbon bonds.[1,2] The process is believed to be promoted by the facile formation of five-membered rings[3] and is also dependent on the steric bulkiness of the phosphine ligands. However, comparatively few examples[4-6] of the intramolecular metalation of the purely aliphatic phosphines are known compared with arylphosphines. Recently, we described intramolecular metalations of tri-*tert*-butylphosphine in platinum[7] and palladium[8] hydrides leading to the formation of $MX(P\text{-}C)(t\text{-}Bu_3P)$ (**1**) (M = Pd, Pt; P-C = $t\text{-}Bu_2PCMe_2CH_2$; X = Cl, Br, I, CF_3CO_2). Compound **1** was also obtained from the reaction of $t\text{-}Bu_3P$ with $PtCl_2(NCPh)_2$ in benzene,[6] although the same reaction in dichloromethane gave the chloro-bridged dimer $[PtCl(P\text{-}C)]_2$ (**2**). Here we discuss possible reaction routes leading to complexes **1** and **2**, as well as the preparation from **2** of several complexes of the type $PtCl(P\text{-}C)L$, L = unidentate ligand.

Results and Discussion

When $t\text{-}Bu_3P$ is allowed to react with $PtCl_2(NCPh)_2$ in a 2:1 molar ratio in dichloromethane, a mixture of $[PtCl(t\text{-}Bu_2PCMe_2CH_2)(t\text{-}Bu_3P)]$ (**1**), $[PtCl(t\text{-}Bu_2PCMe_2CH_2)]_2$ (**2**), and $t\text{-}Bu_3PHCl$ (**3**) is quickly obtained. The reactions described by eq 2–5 are probably involved, leaving eq 1 as the description of the overall reaction.

$$P\text{-}t\text{-}Bu_3 + 2PtCl_2(NCPh)_2 \rightarrow [PtCl(t\text{-}Bu_2PCMe_2CH_2)(t\text{-}Bu_3P)] + [PtCl(t\text{-}Bu_2PCMe_2CH_2)]_2 + t\text{-}Bu_3PHCl \quad (1)$$

$$t\text{-}PBu_3 + PtCl_2(NCPh)_2 \rightarrow Pt(P\text{-}t\text{-}Bu_3)(NCPh)Cl_2 + NCPh \quad (2)$$

$$Pt(P\text{-}t\text{-}Bu_3)(NCPh)Cl_2 \rightarrow {}^1/_2[Pt(P\text{-}t\text{-}Bu_2C(CH_3)_2CH_2)Cl]_2 + HCl + NCPh \quad (3)$$

$$nP\text{-}t\text{-}Bu_3 + nHCl \rightarrow n\,t\text{-}Bu_3PHCl \quad (4)$$

$$(1-n)P\text{-}t\text{-}Bu_3 + {}^1/_2(1-n)[Pt(P\text{-}t\text{-}Bu_2C(CH_3)_2CH_2)Cl]_2 \rightarrow (1-n)PtCl[P\text{-}t\text{-}Bu_2C(CH_3)_2CH_2]P\text{-}t\text{-}Bu_3 \quad (5)$$

As proof of this, the reactions of eq 2–5 have been carried out independently and found to give the expected products. For example, when $t\text{-}Bu_3P$ and $PtCl_2(NCPh)_2$ are allowed to react in a 1:1 molar ratio in CH_2Cl_2, the complex $PtCl_2(NCPh)(t\text{-}Bu_3P)$ (**4**) is obtained. In addition, small amounts of complexes **2** and **3** along with unreacted $PtCl_2(NCPh)_2$ are recovered, suggesting a slow conversion of **4** into **2** (as shown by eq 3). The rate of this conversion of complex **4** into **2** can

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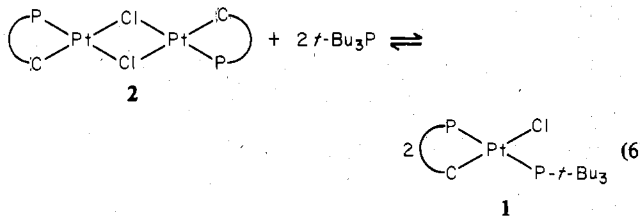
be increased considerably by adding 1 mol more of phosphine. This probably reacts with the HCl which is formed; it may also participate in the reaction of eq 5.

It also appears, from the above results, that the steps represented by eq 3–5 take place almost simultaneously. This is further supported by the fact that the ^{31}P NMR spectrum of the reaction solution of t-Bu$_3$P with $PtCl_2(NCPh)_2$ in a 2:1 molar ratio in CH_2Cl_2 shows all of the signals for complexes **1**, **2**, and t-Bu$_3$PHCl.

Interestingly, when complex **4**, obtained by the reaction of t-Bu$_3$P with $PtCl_2(NCPh)_2$ (eq 2), is treated with ethanol at room temperature, complex **2** is obtained in good yield, within a few minutes.

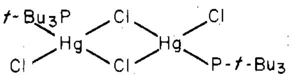
Addition of t-Bu$_3$P to complex **2** leads via the bridge-splitting reaction to complex **1**, although a benzene or dichloromethane solution of **1** reverts to **2** over several days at room temperature. Complexes **1** and **2** are thus related through a solvent-dependent equilibrium (eq 6). The spontaneous reversion of **1** to **2** may be due to oxidation of free phosphine to phosphine oxide or in the case of dichloromethane solutions to slow conversion of phosphine to the phosphonium chloride.



(P-C) = t-Bu$_2$PCMe$_2$CH$_2$

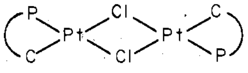
Complex **2** is also obtained when complex **1** is refluxed with $PtCl_2(NCPh)_2$ in benzene for a few minutes, suggesting an alternative route for the formation of **2** in reaction 1. Complex **2** can also be prepared in almost quantitative yield from **1** by treatment with $HgCl_2$ in benzene. This reaction proceeds rapidly at about 50–60 °C, and the resulting products, **2** and $[HgCl_2(t\text{-}Bu_3P)]_2$[10] (eq 7), can be separated easily due to their different solubilities in benzene. Incidentally, the ^{31}P NMR spectrum of the mercury complex $[HgCl_2(t\text{-}Bu_3P)]_2$ shows a singlet at δ +96.30 with J(HgP) = 6754 Hz.

[PtCl(t-Bu$_2$PCMe$_2$CH$_2$)(t-Bu$_3$P)] + HgCl$_2$ → **2** +

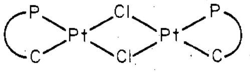


(7)

The ^{1}H NMR spectrum of **2** in dichloromethane shows two sets of doublets at δ 1.50 [J(P–C–C–H) = 13.8 Hz] and δ 1.46 [J(P–C–C–H) = 14.4 Hz] in a 3:1 intensity ratio due to the *tert*-butyl (t-Bu$_2$P) and methyl (CMe$_2$) protons, respectively, along with two weak signals due to methylene (CH$_2$–Pt) protons at δ 1.40 [J(P–C–C–H) = 6.5 and $J(^{195}$Pt–H) = 128 Hz]. The ^{31}P NMR spectrum of **2** (in CDCl$_3$) shows a triplet consisting of a main peak (δ −18.6) and two satellite peaks due to ^{195}Pt–^{31}P spin–spin coupling [J(Pt–P) = 3757 Hz]. However upon further resolution of this spectrum, another set of less intense signals can also be observed at δ −18.8 [J(Pt–P) = 3793 Hz]. These ^{31}P NMR spectral results suggest the presence of both symmetrical (**2a**) and antisymmetrical (**2b**) isomers.[11] They are also apparent in the ^{31}P NMR spectrum of the complex run in CH$_2$Cl$_2$ solution, which shows two sets of signals at δ −16.38 [J(PtP) = 3759 Hz] and δ −15.98 [J(PtP) = 3740 Hz], suggesting a solvent effect.



2a



2b

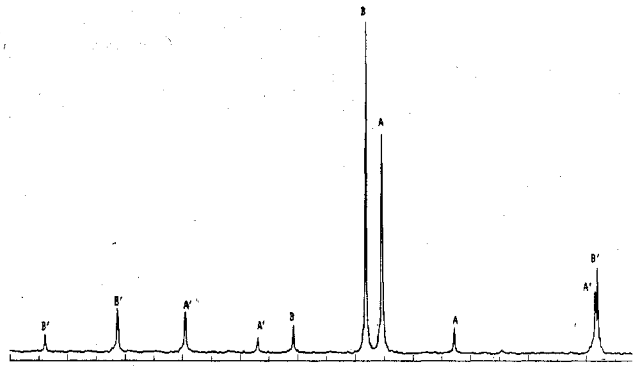
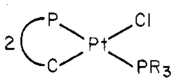


Figure 1. ^{31}P NMR spectrum of PtCl(P-C)(PEt$_3$), where (P-C) = (t-Bu$_2$PCMe$_2$CH$_2$), in CH$_2$Cl$_2$ at −90 °C. Signals AA are due to the metalated *tert*-butylphosphine coupled with PEt$_3$ [J(PP′) = A–A], and the platinum satellites are A′A′. Similarly, BB are the main signals due to PEt$_3$ coupled with metalated *tert*-butylphosphine with B′B′ as platinum satellites.

Preparation of Mixed-Ligand Complexes by Bridge-Splitting Reactions. Various types of ligands cleave[2] the chlorine bridge of the dimeric complex [PtCl(t-Bu$_2$PCMe$_2$CH$_2$)]$_2$ (**2**), resulting in the formation of mixed-ligand complexes,[12] PtCl(t-Bu$_2$PCMe$_2$CH$_2$)L (**5**). Their geometry depends on the nature of the ligands. When tertiary phosphines are added to benzene solutions of **2**, complexes of the type *trans*-PtCl(P-C)(PR$_3$) (**5**) are obtained in almost quantitative yields (eq 8). The stabilities of these complexes are related to the steric bulkiness of the phosphine, and, for PR$_3$ = t-Bu$_3$P, **5** dissociates upon standing in solution (CH$_2$Cl$_2$ or benzene) to give **2** and free phosphine. However, the complexes containing less bulky phosphines (PR$_3$ = Et$_3$P, Ph$_2$MeP, Ph$_3$P, i-Pr$_3$P, t-BuPh$_2$P, t-Bu$_2$MeP, c-Hx$_3$P) seem to be stable in solution for at least 1 week.

[PtCl(t-Bu$_2$PCMe$_2$CH$_2$)]$_2$ + 2PR$_3$ → 2



(8)

The trans configuration of these species has been ascertained on the basis of their ^{31}P NMR spectra which show a large phosphorus–phosphorus coupling [J(PP′)] (due to magnetically nonequivalent phosphorus nuclei) of the order of 383–424 Hz.[13] With two such phosphorus nuclei, a 12-line spectrum is observed in all the cases (each phosphorus gives a doublet with ^{195}Pt satellites) (Table I), except in the case of the complex *trans*-PtCl(P-C)(PEt$_3$), where, instead of 12 lines, only 10 lines are observed. In the spectrum, the two phosphine signals appear as doublets centered at δ −3.12 [P(metalated)] and δ +16.59 [P(PEt$_3$)] with J(PP′) = 415 Hz. The ^{195}Pt satellites toward the lower field of the main doublet signals appear as the expected doublets; however, the satellites toward the high field are observed as singlets. This pattern is observed at various temperatures as well as in different solvents (Table I) and is also independent of the instrument being used. The explanation for this irregular behavior is not clear, but it is interesting that the sum of $^1/_2J$(PtP) + $^1/_2J$(PtP′) (low field) obtained by taking the mean values is equal to the sum of $^1/_2J$(PtP) + $^1/_2J$(PtP′) (high field) (see Figure 1). Another irregularity which cannot be fully explained is noticed in the ^{31}P spectrum of PtCl(P-C)(Ph$_2$MeP) which shows only three lines. As suggested in Table I, this may be attributed to an

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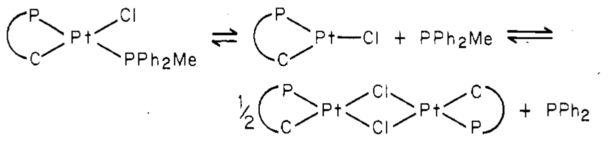
Table I. ^{31}P NMR Spectral Data of PtCl(P-C)L

		metalated phosphine		unmetalated phosphine		
no.	PtCl(P-C)L	δ(P)	*J*(PtP), Hz	δ(P)	*J*(PtP), Hz	*J*(PP′) Hz
1a	$[PtCl(P\text{-}C)]_2$	−18.8	3793			
		−18.6	3757			
1b	$[PtCl(P\text{-}C)]_2$	−16.4	3759			
		−16.0	3740			
2a	$[PtCl(P\text{-}C)](PEt_3)$	+2.0	2207	+22.4	2793	410
			2300		2695	
2b	$PtCl(P\text{-}C)(PEt_3)$	−3.1	2271	+16.6	2788	415
			2356		2698	
2c	$PtCl(P\text{-}C)(PEt_3)$	−4.3	2266	+16.4	2793	422
			2349		2703	
3a	$PtCl(P\text{-}C)(P\text{-}i\text{-}Pr_3)$	−2.9	2228	+34.5	2822	393
3b	$PtCl(P\text{-}C)(P\text{-}i\text{-}Pr_3)$	−4.1	2219	+34.7	2839	400
4	$PtCl(P\text{-}C)(P\text{-}c\text{-}Hx_3)$	−4.8	2251	+24.3	2776	400
5	$PtCl(P\text{-}C)(P\text{-}t\text{-}Bu_2Me)$	−8.2	2285	+27.3	2852	405
6	$PtCl(P\text{-}C)(P\text{-}t\text{-}Bu_3)$	−12.8	2360	+66.8	2680	383
7	$PtCl(P\text{-}C)(PPh_2Me)$	−11.3	2942	−11.3	2942	
8	$PtCl(P\text{-}C)(PPh_3)$	−10.7	2400	+23.3	2852	424
9	$PtCl(P\text{-}C)(PPh_2\text{-}t\text{-}Bu)$	−9.3	2363	+38.3	2896	405
10a	*cis*-$PtCl(P\text{-}C)(P(OPh)_3)$	−11.7	3179	+123.4	3300	7.80
10b	*trans*-$PtCl(P\text{-}C)[P(OPh)_3]$	−5.7	2319	+106.2	5026	635
11	$PtCl(P\text{-}C)(AsPh_3)$	−11.4	2940			
12a	*cis*-$PtCl(P\text{-}C)(SbPh_3)$	−11.4	3184			
12b	*trans*-$PtCl(P\text{-}C)(SbPh_3)$	−6.8	3142			
13	$PtCl(P\text{-}C)(CO)$	−10.9	2791			
14	$PtCl(P\text{-}C)(py)$	−19.8	3233			
15	$PtCl(P\text{-}C)(Me_2S)$	−11.7	3214			

[a] (P-C) = (t-$Bu_2PCMe_2CH_2$); py = pyridine. All spectra were recorded in benzene except those of **1a** (in $CDCl_3$), **1b** and **15** (in CH_2Cl_2), **2a** (in CH_2Cl at −90 °C), and **2b**, **3a**, **9**, and **10** (in $CDCl_3$) at room temperature.

unlikely but accidental degeneracy of both δ(P) and *J*(PtP) for the two phosphines. It also requires no coupling between the two P nuclei, probably due to a rapid exchange between two complexes as shown in eq 9. However, the spectrum at −60 °C was unchanged.



(9)

In these complexes the metalated phosphine is a constant component for one "side" of each molecule.

The values for *J*[PtP(metalated)] may well then reflect only the effect of the phosphine ligand of the trans position (i.e., trans influence of the phosphine ligand).[14,15] Upon examination of these values (Table I), it is observed that in the series of alkylphosphines (P-i-Pr_3—P-t-Bu_3), as the size of the ligand increases, the *J*[PtP(metalated)] value increases, suggesting a decreasing order of trans influence (i.e., when the size order[14] is P-i-Pr_3 < P-t-Bu_2Me < t-Bu_3P, then the trans-influence order is P-i-Pr_3 > P-t-Bu_2Me > t-Bu_3P). If this generalization is true, then since triethylphosphine is smaller than i-Pr_3P, its trans influence should be larger than that of i-Pr_3P, and hence the value of *J*(PtP) should be smaller. However, the value of *J*(PtP) for PEt_3 is found to be the larger.

It must, however, be emphasized that the *J*(PtP) value being used here is derived from a spectrum which, as described above, shows irregular and unexplained features.

For arylphosphine ligands, the dominant factor for trans influence appears to be electronic rather than steric.[16] For example, *J*[PtP(metalated)] observed for the complex *trans*-PtCl(P-C)(Ph_3P) is 2400 Hz, larger than the values found for any trialkylphosphine complexes regardless of the size of the phosphine. Hence, this large value of *J*(PtP) is probably due to the electronic parameter of PPh_3 which is known[16] to differ from that of alkylphosphines. Similarly, the lower value of *J*(PtP) for PPh_2-t-Bu compared to that for Ph_3P suggests a greater trans influence for Ph_2-t-BuP than for Ph_3P, and this difference cannot be explained just on the basis of the steric size of the phosphine.

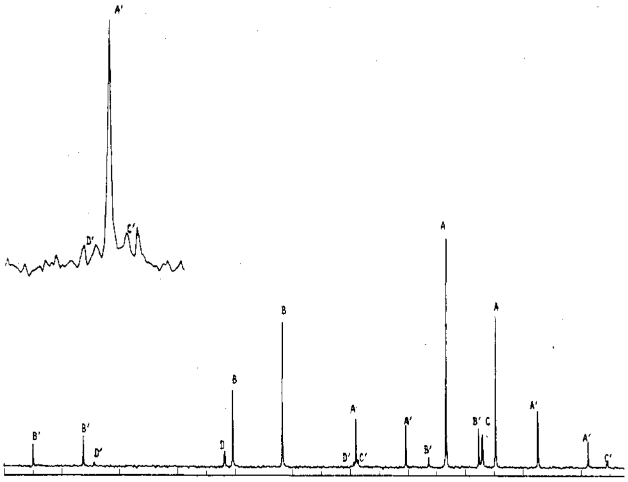


Figure 2. ^{31}P NMR spectrum of a mixture of *cis*- and *trans*-PtCl(P-C)P$(OPh)_3$. AA are the main signals due to metalated *tert*-butylphosphine of the trans complex [*J*(PP′) = A–A] with platinum satellites (shown by A′). Signals BB are due to $P(OPh)_3$ with B′B′ as platinum satellites. The doublets shown by C and D, which are due to the cis complex, are the main peaks due to metalated *tert*-butylphosphine and $P(OPh)_3$, respectively, with platinum satellites shown by C′ and D′.

When triphenyl phosphite is allowed to react with the dimeric complex **2**, a mixture of products *trans*-PtCl(P-C)-$(PhO)_3P$ (major) and *cis*-PtCl(P-C)$(PhO)_3P$ (minor) is obtained (eq 10), characterized by the ^{31}P NMR spectrum (Figure 2) which shows, besides the 12 lines due to the trans complex, six more doublets (*J*(PP′) = 7.8 Hz) due to the cis

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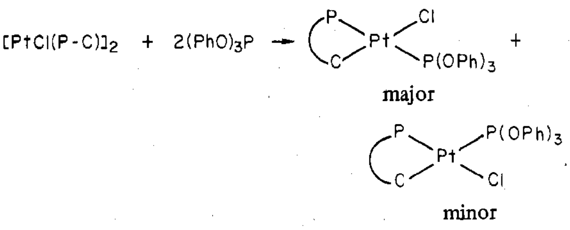

(10)

complex at δ[P(metalated)] −11.71 [J(PtP) = 3179 Hz] and δ(P′) +123.39 [J(PtP) = 3301 Hz]. The J[PtP(m)] value (P(m) is phosphorus of metalated phosphine) observed (2319 Hz) for the trans complex suggests that the trans influence of $(PhO)_3P$ is greater than that of Ph_3P, which is contrary to the results observed by Allen et al.[12] in the series of complexes *trans*-PtCl(n-Bu_3P)L. The reaction of Ph_3As with complex **2** results in the formation of *trans*-PtCl(P-C)(Ph_3As). However, when Ph_3Sb is allowed to react with **2**, both *cis*- and *trans*-PtCl(P-C)(Ph_3Sb) are obtained as observed in the ^{31}P NMR spectrum. Carbon monoxide undergoes the bridge-cleavage reaction with complex **2**, smoothly at room temperature unlike the palladium analogues for which no such reaction is observed,[8] to give a complex with the trans configuration. Similarly, pyridine reacts with the dimer complex **2**, giving only the trans product, contrary to earlier reports for $[PtCl(P-C)]_2$ [where (P-C) = t-$Bu_2PC_6H_4CH_2$ or $CH_2C_6H_4P$-t-Bu(o-tol)] where both cis and trans complexes have been prepared.[3] Dimethyl sulfide reacts with the dimeric complex **2** to give a cis product which is unstable in solution and dissociates, giving back the starting material **2** (eq 11).

$$[PtCl(P\text{-}C)]_2 + 2Me_2S \rightleftharpoons PtCl(P\text{-}C)(Me_2S) \qquad (11)$$

From the values of J(PtP) observed in the above complexes (Table I) we find a trend for the trans influence of the ligands used in this present investigation as follows: i-Pr_3P > c-Hx_3P > t-Bu_2MeP > $(PhO)_3P$ > t-Bu_3P > Ph_2-t-BuP > Ph_3P > CO > Ph_3As > Ph_3Sb > py. We have not included Et_3P and Ph_2MeP in this series because of the irregular spectra observed for these complexes.

The ^1H NMR spectral parameters for complexes PtCl(P-C)L (**5**) are given in Table II. Where L is other than a phosphine ligand, the metalated phosphine shows signals due to *tert*-butyl (t-Bu_2P) and methyl (CMe_2) protons as doublets in the ratio 3:1. The methylene protons are also observable as a doublet with ^{195}Pt satellites. For example, complex **5** (L = pyridine) shows doublets due to *tert*-butyl and methyl groups at δ 1.55 [^3J(P–H) = 13.5 Hz] and δ 1.55 [J(P–H) = 13.6 Hz], respectively. The methylene proton signals are observed at δ 1.27 as a doublet [J(PH) = 7.9 Hz] with platinum satellites [J(PtH) = 102 Hz]. Some of the spectra for complexes containing two magnetically nonequivalent phosphines at positions trans with respect to each other, e.g., *trans*-PtCl(P-C)(PR_3), show signals due to the *tert*-butyl and methyl group protons as double doublets due to the splitting by both phosphorus nuclei. The methylene proton signals are observed as two sets of doublets. In particular, the spectrum of complex **5** (R_3P = Ph_3P) shows double doublets due to the *tert*-butyl groups at δ 1.54 [^3J(PH) = 12.2 Hz and ^5J(PH) = 1.0 Hz] and due to methyl protons at δ 1.30 [^3J(PH) = 12.0 Hz and ^5J(PH) = 1.0 Hz]. The methylene protons (C–CH_2–Pt) are observed as two doublets at δ 0.83 and 0.98 [J(PH) = 5.0 Hz] with J(PtH) = 94 Hz.

Experimental Section

Tri-*tert*-butylphosphine was prepared as described previously[17] and distilled under reduced pressure at 58–60 °C (0.1 mm). All other phosphines were obtained from Strem Chemicals Inc. All operations involved in the reactions of t-Bu_3P and other air-sensitive phosphines such as t-Bu_2MeP, t-Ph_2BuP, Ph_2MeP, etc. were carried out under a nitrogen atmosphere with the use of Schlenk-tube techniques. All the solvents used were of spectroanalyzed grade and were degassed prior to use. Platinum(II) chloride was obtained from Johnson, Matthey, and Mallory, Ltd.; $PtCl_2(NCPh)_2$ was prepared by refluxing $PtCl_2$ in excess benzonitrile and was crystallized from CH_2Cl_2/hexane.

Elemental analyses were performed by M.H.W. Laboratories, Phoenix, Ariz. Infrared spectra were recorded on a Beckman IR-12 spectrophotometer using CsI plates in Nujol. ^1H NMR spectra were recorded on a Varian A-60 spectrophotometer, and ^{31}P NMR spectra were obtained with a Bruker 60 Fourier transform spectrometer. Me_4Si was used as an internal standard for ^1H NMR spectra and external H_3PO_4 for ^{31}P NMR spectra. Melting points were determined with a Gallenkamp melting point apparatus in glass capillary tubes and are uncorrected.

Reaction of t-Bu_3P with $PtCl_2(NCPh)_2$ in CH_2Cl_2. (a) Molar Ratio 1:1. To a magnetically stirred solution of $PtCl_2(NCPh)_2$ (3.78 g; 8.0 mmol) in 70 mL of CH_2Cl_2 was added dropwise t-Bu_3P (1.60 g; 8.0 mmol), and the reaction mixture was stirred at room temperature for ≃4 h during which time the color of the solution changed from yellow to orange-red. Solvent was stripped off under reduced pressure to give a viscous paste. A 30-mL sample of 95% ethanol was added, and the mixture was stirred for ≃30 min to give a pale white, insoluble solid which was filtered and dissolved in benzene. From this benzene solution, colorless prism-shaped crystals were obtained by the addition of hexane. The yield of the reaction varied from 55 to 85% depending upon the length of time of the reactions. Anal. Calcd for $[PtCl(t\text{-}Bu_2PCMe_2CH_2)]_2$: C, 33.40; H, 6.03; Cl, 8.23; mol wt 863. Found: C, 33.30; H, 6.03; Cl, 8.22; mol wt 856 (in benzene). Mp: 212–215 °C (sample started turning grayish black at 212 °C and melted at 230 °C).

(b) Molar Ratio 2:1. t-Bu_3P (1.62 g; 8.0 mmol) was added dropwise to a well-stirred solution of $PtCl_2(NCPh)_2$ (1.89 g; 4.0 mmol) in CH_2Cl_2 (50 mL) at room temperature under nitrogen. The reaction solution was allowed to react for ≃2 h. The solvent was removed under reduced pressure, and the resulting product was dried in vacuo for ≃1 h at 50–60 °C. The pale white solid was treated with hexane and the mixture filtered.

The hexane-soluble fraction was concentrated to give a white crystalline solid, yield 40%. Anal. Calcd for $PtCl[P\text{-}t\text{-}Bu_2C(CH_3)_2CH_2](P\text{-}t\text{-}Bu_3)$: C, 45.44; H, 8.43; Cl, 5.60. Found: C, 45.40; H, 8.41; Cl, 5.62. The hexane-insoluble solid was washed with ethanol, and the white insoluble solid was recrystallized from a benzene/hexane mixture; yield 36%. Anal. Calcd for $[Pt(P\text{-}t\text{-}Bu_2C(CH_3)_2CH_2)Cl]_2$: C, 33.40; H, 6.03; Cl, 8.23; mol wt 863. Found: C, 33.30; H, 6.02; Cl, 8.23; mol wt 851 (in benzene). The ethanol-soluble fraction was evaporated and washed with hexane to give a white solid which was characterized as t-Bu_3PHCl by its infrared (ν(PH) 2382 cm^{-1}) and ^1H and ^{31}P NMR spectra.[2]

Reaction of $PtCl(t\text{-}Bu_2PCMe_2)(t\text{-}Bu_3P)$ with $PtCl_2(NCPh)_2$. $PtCl(t\text{-}Bu_2PCMe_2CH_2)(t\text{-}Bu_3P)$ (1.5 mmol) and $PtCl_2(NCPh)_2$ (1.5 mmol) were mixed together in benzene (≃35 mL), and the reaction mixture was refluxed for ≃3 h to give a clear solution. Solvent was removed, the resulting solid was washed with ethanol, and the residue was crystallized from benzene/hexane. The product corresponded analytically to the dimeric complex **2**.

Reaction between $PtCl(t\text{-}Bu_2PCMe_2CH_2)(P\text{-}t\text{-}Bu_3)$ (1) and $HgCl_2$. To a solution of the complex **1** (1.0 mmol) in benzene (≃25 mL) was added mercury(II) chloride (1.0 mmol). The reaction mixture was stirred for about 2 h at 60 °C, and after it cooled to room temperature, the white crystalline solid which separated was filtered off. The filtrate was concentrated, and the product was crystallized by the addition of hexane. Both benzene-soluble and -insoluble solids were analyzed and characterized by ^1H and ^{31}P NMR spectra. Anal. Calcd for $[(t\text{-}Bu_3P)HgCl_2]_2$: C, 30.41; H, 5.70; Cl, 14.99. Found for benzene-insoluble solid: C, 30.52; H, 5.68; Cl, 15.23. The benzene-soluble product was found to be complex **2**, characterized by its elemental analyses and ^1H and ^{31}P NMR spectra.

Bridge-Splitting Reactions of $[PtCl(t\text{-}Bu_2PCMe_2CH_2)]_2$. (a) With Trialkyl- or Triarylphosphines, Triphenylarsine, and Triphenylstibine. Typically, to a solution of the dimeric complex $[PtCl(t\text{-}Bu_2PCMe_2CH_2)]_2$ in benzene was added an equimolar amount of triphenylphosphine, and the reaction mixture was allowed to react for 2–3 h at 60 °C. After concentration of the solution, crystals of the compound $PtCl(t\text{-}Bu_2PCMe_2CH_2)(Ph_3P)$ (**5**) were obtained by

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Table II. ^{1}H NMR Spectral Data of PtCl(CH_2C_3P-*t*-Bu_2)L[a]

	signals due to CH_2CMe_2P-*t*-Bu_2								
	tert-butyl (P-*t*-Bu_2)			dimethyl (P-CMe_2)		methylene (P-C-CH_2Pt)			
L	δ(*t*-Bu)	^3J(P-H) or "*J*"(P-H), Hz	^5J(P-H), Hz	δ(Me)	^3J(P-H) or "*J*"(P-H), Hz	δ(CH_2)	*J*(P-H), Hz	*J*(Pt-H), Hz	signals due to ligand: δ [*J*(P-H), Hz]
t-Bu_2MeP	1.62 (d)	13.5		1.55 (d)	12.5	1.06 (d) 0.88 (d)	5.2 5.2	92	*t*-Bu 1.42 [*J*(P-H) = 11]; Me 1.50 (t) [*J*(P-H) = 5.6]
Ph_3P	1.54 (dd)	12.2	1.0	1.30 (dd)	12.0 [^5J(P-H) = 1.0]	0.83 (d) 0.98 (d)	5.0 5.0	94	Ph 7.17 (m), 7.90 (m)
Ph_3P[b]	1.58 (d)	12.3		1.35 (d)	11.5	0.82 (d) 0.64 (d)	5.0 5.0	94	Ph 7.18 (m), 7.90 (m)
Ph_2-*t*-BuP	1.68 (dd)	12.2	1.0	1.50 (d)	11.6	1.01 (d) 1.15	5.0 5.0	94	Ph 7.20 (m, b), 7.86 (m, b)
CO	1.09 (d)	14.4		1.23 (d)	15.8	1.58 (d)	9.3	87.5	
trans-$SbPh_3$	1.60 (d)	13.1		1.46 (d)	14	1.62	8.9	89	Ph 7.48 (m)
cis-$SbPh_3$	1.36 (d)	13		1.54 (d)	14	1.39	9.0	90	Ph 7.48 (m)
Ph_3As	1.62 (d)	14		1.38 (d)	12	0.88 (d)	9.5	92	Ph 7.45 (m), 7.76 (m)
Ph_2MeP	1.50 (dd)	9.5	3.0	1.34 (dd)	10.0 [^5J(P-H) = 3.0]	0.87 (d) 0.72 (d)	6.6 6.8	95	Me 1.98 (d) [*J*(P-H) = 6, *J*(Pt-H) = 26]; Ph 7.40 (m); 7.70 (m)
i-Pr_3P	1.62 (d)	13		1.38 (d)	12.3	"a"			CH_3 1.17 (t) [*J*(PH) = 6.9]; CH 2.36 (m)
py	1.55 (d)	13.5		1.50 (d)	13.6	1.27 (d)	7.8	102	py 7.2-7.8 (m)
Me_2S[b]	1.45 (d)	14		1.53	13.8	1.43	8.5	90	2.47 (s) [*J*(PtH) = 22]
c-Hx_3P	1.43 (d)	11.2		1.53 (d)	12.7	1.04 (d) 1.20 (d)	5.0	92	1.5 (b)
t-Bu_3P	1.66 (d)	13		1.81 (d)	12	"a"			1.71 (d) [*J*(PH) = 11.5]
Et_3P	1.38 (d)	11.7		1.54 (d)	12.6	"a"			CH_3 1.28 (q); CH_2 1.386 (m)

[a] All spectra were recorded in C_6D_6 except as noted otherwise. d = doublet. "a": signals due to -CH_2 cannot be observed due to other strong signals. [b] Spectra were recorded in $CDCl_3$.

Table III. Physical and Analytical Data of PtCl[$CH_2C(CH_3)_2P$-*t*-Bu_2]L

				anal., %						
no.	ligand	solvent of crystn	yield, %	calcd	found	calcd	found	calcd	found	mp, °C
1	CO	benzene/hexane	92	33.95	33.80	5.66	5.62	7.73	7.85	145
2	Et_3P	ethanol/H_2O	74	39.31	39.40	7.46	7.45	6.46	6.59	85
3	Ph_2MeP	benzene/hexane or ethanol/H_2O	80	47.51	47.25	6.18	6.10	5.62	5.95	178
4	Ph_3P	benzene/ethanol or benzene/hexane	90	51.91	51.83	5.91	5.88	5.12	5.21	205
5	Ph_3As	benzene/ethanol or benzene/hexane	92	48.79	48.80	5.56	5.51	4.81	4.85	202
6	Ph_3Sb	benzene/hexane	89	45.91	46.01	5.23	5.19	4.53	4.58	195 dec
7	*i*-Pr_3P	benzene/hexane	85	42.60	42.31	7.79	7.85	6.00	6.05	160
8	c-Hx_3P	ethanol/H_2O	82	50.60	50.55	8.29	8.18	4.99	4.95	203
9	Ph_2-*t*-BuP	CH_2Cl_2/hexane	80	43.44	43.40	5.82	5.87	4.59	4.79	203-205
10	*t*-Bu_2MeP	benzene/ethanol/H_2O	80	42.60	42.39	7.95	7.94	6.00	6.21	183-185
11	*t*-Bu_3P	hexane	85	45.46	45.40	8.37	8.32	5.60	5.72	239 dec
12	C_5H_5N	cold hexane	85	39.96	40.05	6.07	6.01	6.95	7.04	142
13	Me_2S		88[a]	34.04	33.98	6.48	6.47	7.19	7.21	230 dec
14	$(PhO)_3P$	benzene/hexane	82	48.55	48.62	5.53	5.52	4.79	4.81	
15	[PtCl(P-C)]$_2$	benzene/hexane	*b*	33.40	33.30	6.03	6.03	8.23	8.22	212-215 dec

[a] Yield before crystallization. [b] Yield varies with methods of preparation.

the addition of hexane. Analyses of this complex and other complexes prepared similarly by using ligands Et_3P, Ph_2MeP, *i*-Pr_3P, Ph_2-*t*-BuP, *t*-Bu_2MeP, *t*-Bu_3P, c-Hx_3P, $(PhO)_3P$, Ph_3As, and Ph_3Sb are given in Table III.

(b) With Pyridine. An excess of pyridine was added to the solution of dimeric complex **2** in benzene, and the reaction mixture was warmed to 60 °C and allowed to react for ≃2 h. Solvent was removed, and the residue was recrystallized from cold hexane to give flakelike white crystals. Analyses are given in the Table III.

(c) With Carbon Monoxide. A stream of carbon monoxide was bubbled through a benzene solution of dimeric complex **2** at room temperature for ≃$^1/_2$ h, and the product was crystallized as colorless prisms from a benzene/hexane mixture. The infrared spectrum of the complex $PtCl(t\text{-}Bu_2PCMe_2CH_2)(CO)$ showed a band of 2055 cm^{-1} due to a terminal carbonyl group. Analytical and spectral data of the complex are given in the tables.

(d) With Dimethyl Sulfide. To a solution of dimeric complex **1** in benzene was added an excess of dimethyl sulfide, and the reaction mixture was stirred at room temperature for ≃3 h. The solvent was removed, and the proton NMR spectrum of the resulting product was recorded in $CDCl_3$. This showed the presence of 1 molar equiv of Me_2S complexed to platinum, confirmed by the appearance of ^{195}Pt satellites [$J(Pt–H) = 22$ Hz] for the methyl signals. During the attempted crystallization of the complex from benzene/hexane, dimethyl sulfide was found to be displaced and the starting material **2** crystallized out.

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Registry No. 1, 63230-78-4; **2a**, 74523-69-6; **2b**, 74523-70-9; **5** (L = PEt_3), 74482-66-9; **5** (L = $P\text{-}i\text{-}Pr_3$), 74482-67-0; **5** (L = $P\text{-}c\text{-}Hx_3$), 74482-68-1; **5** (L = $P\text{-}t\text{-}Bu_2Me$), 74482-69-2; **5** (L = PPh_2Me), 74482-70-5; **5** (L = PPh_3), 74482-71-6; **5** (L = $PPh_2\text{-}t\text{-}Bu$), 74482-72-7; **5** (L = $AsPh_3$), 74482-73-8; **5** (L = CO), 74482-74-9; **5** (L = py), 74482-75-0; **5** (L = Me_2S), 74482-76-1; *cis*-$PtCl(P\text{-}C)(P(OPh)_3)$, 74482-77-2; *trans*-$PtCl(P\text{-}C)(P(OPh)_3)$, 74523-71-0; *cis*-$PtCl(P\text{-}C)(SbPh_3)$, 74482-78-3; *trans*-$PtCl(P\text{-}C)(SbPh_3)$, 74559-66-3; *trans*-$PtCl_2(NCPh)_2$, 51921-56-3; $[(Bu_3P)HgCl_2]_2$, 41665-95-6; *t*-Bu_3PHCl, 63197-35-3.

Contribution from the Department of Chemistry,
Oregon State University, Corvallis, Oregon 97331

Evidence for Cobalt(II) Catalysis and for an Intermediate Dioxygen Adduct in the Autoxidation of Cobalt(II) Chloride Complexes of Ethyl Phosphinite, Phosphonite, and Phosphite Esters[1]

WEN-SHU HWANG, INGO B. JOEDICKE, and JOHN T. YOKE*

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With use of the ligands $L = Et_nP(OEt)_{3-n}$, $n = 0–2$, the equilibrium constants and thermodynamic functions have been determined for the high-spin low-spin equilibria $CoCl_2L_2 + L \rightleftharpoons CoCl_2L_3$ in benzene. In the autoxidation both of $CoCl_2L_2$ complexes and of $CoCl_2L_3 \rightleftharpoons CoCl_2L_2 + L$ equilibrium systems, all the L is converted to its phosphoryl derivative LO with no change in the value of *n*. In their initial stages the reactions are first order in cobalt complex; first-order dependence on oxygen was demonstrated in representative cases. The autoxidation rate constants for the high-spin $CoCl_2L_2$ complexes and the low-spin $CoCl_2L_3$ complexes are not very different; autoxidation of $CoCl_2(Et_3P)_2$ is 1 order of magnitude slower. For the $n = 1$ system, the 1:1 dioxygen adduct intermediate was prepared at a low temperature, and the stoichiometry and kinetics of its irreversible rearrangement were determined. In the proposed autoxidation mechanism, formation of the dioxygen adduct is the rate-determining step. Ligand redistribution equilibria make kinetics complex in the latter stages of the autoxidation. A catalytic cycle has been demonstrated in the autoxidation of triethyl phosphite under mild conditions.

Introduction

Tertiary aliphatic phosphines and phosphorus esters, $R_nP(OR)_{3-n}$, $n = 0–3$, react with dioxygen by a radical chain mechanism to give phosphoryl oxidation products.[2] With free radical or photoinitiation, tertiary phosphites ($n = 0$) are oxidized quantitatively to phosphates $P(O)(OR)_3$, but all the others give a mixture of oxidation products. For example, a phosphinite ester R_2POR gives some $RP(OR)_2$ and $P(OR)_3$ intermediates and $R_2P(O)OR$, $RP(O)(OR)_2$, and $P(O)(OR)_3$ final products.[3] This is because the mechanism[2] involves formation of intermediate phosphoranyl radicals, e.g., eq 1,

$$RO\cdot + R_2POR \rightarrow R_2\dot{P}(OR)_2 \qquad (1)$$

which can decompose either by C–O bond rupture (eq 2a) to give a final phosphoryl product or by C–P bond rupture (eq 2b) to give a new trivalent phosphorus intermediate subject to further oxidation.

$$R_2\dot{P}(OR)_2 \rightarrow R_2P(O)OR + R\cdot \qquad (2a)$$

$$\rightarrow RP(OR)_2 + R\cdot \qquad (2b)$$

In contrast, it has been shown[4] that triethylphosphine in its cobalt(II) chloride complex $CoCl_2(Et_3P)_2$, in organic solvents, is oxidized quantitatively to the phosphine oxide complex $CoCl_2(Et_3PO)_2$ by a nonradical pathway. The proposed mechanism involves formation and decomposition of an intermediate cobalt(II)–dioxygen adduct, eq 3.

$$CoCl_2(Et_3P)_2 + O_2 \rightarrow O_2CoCl_2(Et_3P)_2 \rightarrow CoCl_2(Et_3PO)_2 \qquad (3)$$

Triethylphosphine has the largest steric requirement of the four $Et_nP(OEt)_{3-n}$ ligands.[5] Its only cobalt(II) chloride complex is $CoCl_2(Et_3P)_2$, as has been shown by studies of the solid–vapor equilibrium system[6] and of solutions of the components in organic solvents.[7] It alone fails to participate in the high-spin (quartet state) low-spin (doublet state) equilibrium reactions, eq 4, the equilibrium constants for which

$$CoCl_2L_2 + L \rightleftharpoons CoCl_2L_3 \qquad (4)$$

have been reported[8] in *tert*-butylbenzene solution with the ligands $L = Et_nP(OEt)_{3-n}$, $n = 0–2$. All three types of species in the equilibrium mixture are susceptible to autoxidation. It is of interest to see what effect the differences in cobalt paramagnetism and coordination number will have on the rates and products of the reaction with dioxygen and to see if cobalt(II) chloride can bring about oxidation of large amounts of substrate in a catalytic cycle, as well as of stoichiometric amounts in the complexes. The postulated role of a cobalt–dioxygen adduct is also to be investigated. In all cases except $n = 0$, there is the possibility that autoxidation of free phosphorus ligand can be distinguished from autoxidation of coordinated ligand by detection of mixed phosphoryl products,

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